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FULL PAPER

Methionine-functionalized chitosan–Pd(0) complex: A novel magnetically separable catalyst for Heck reaction of aryl iodides and aryl bromides at room temperature in water as only solvent

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We report a novel catalyst system with an immobilized palladium metal-containing magnetic nanoparticle core (ImmPd(0)-MNPs) for the Heck reaction. ImmPd(0)-MNPs was found to be an exceptionally mild and versatile catalyst for the Heck reaction of aryl iodides and bromides at room temperature. The catalyst was simply recovered using an external magnet from the reaction mixture and recycled six times. The results showed that the catalyst was very active and stable. Moreover, the reaction was carried out in water as a green and environmentally acceptable solvent. In terms of scope and mildness, ImmPd(0)-MNPs is an improvement over previously reported catalysts for Heck coupling methods.

KEYWORDS

Heck reaction, ImmPd(0)-MNPs, room temperature, water

1 | INTRODUCTION

One of the most challenging tasks in organic chemistry is to design convenient routes for cross-coupling reactions including reusable, efficient and green catalysts.[1] With the final goal of solving environmental problems, the use of water and its co-solvents as the reaction media instead of toxic organic solvents has gained high importance in the field of catalysis.[2] In the context of green chemistry, a convenient route for cross-coupling reactions involves reusable palladium nanoparticles that promote these reactions in green solvents.[3–5] Homogeneous palladium catalysts used in these reactions have several drawbacks such as time-consuming work-up procedures attendant with inefficient recycling. A heterogeneous palladium catalyst can solve these problems.[6–13] Metal nanoparticles have become attractive tools for catalysis because of their high surface area-to-volume ratio. A key challenge in the application of these catalysts is accumulation of nanoparticles, which may lead to deactivation.[14,15] Furthermore, isolation and recovery of heterogeneous catalysts from a reaction mixture become difficult as their size decreases to the nanoscale. Thus, magnetic nanoparticles (MNPs) which have emerged as bridges between homogeneous and heterogeneous catalysts can be used as appropriate support materials to develop highly efficient recycling methods for catalysts. They possess some advantages which make them more sustainable, such as easy separation using an external magnet, high reactivity, very high surface area-to-volume ratio, and high thermal and mechanical stability. Because of these advantages, recent advances have led to the use of magnetically recoverable catalysts in coupling reactions.[16–18] Development of MNP-supported catalysts depends on two features: primarily, the synthesis of size-controlled and mono-dispersed MNPs;[17,19] secondly, avoiding the aggregation of MNPs through their surface stabilization. Thus, using an appropriate surface modification for MNPs can help to achieve stability and well-dispersed active species.

In recent years, a variety of polymeric support materials have been used as catalyst carriers in chemical reactions.[20–22] As one kind of widely used biopolymers, chitosan which has two types of reactive functional groups, amino groups and hydroxyl groups,[23] has been used as a suitable solid support for the immobilization of a metal catalyst.[24] The main disadvantages of chitosan, which significantly limit its use as an effective and recyclable biopolymer, are poor chemical resistance and mechanical strength. Accordingly, it is often necessary to use a stronger ligand to help bind the metals more strongly for catalytic applications. From the point of view of biodegradability, implanting of amino acids[25–27] to chitosan via carbodiimide coupling protocols would result in amphiphilic derivatives, which improve the formation of nanoscale micellar structures in aqueous environments. Previously, we reported proline-functionalized chitosan–palladium(II) as an efficient catalyst for the Suzuki reaction.[28]

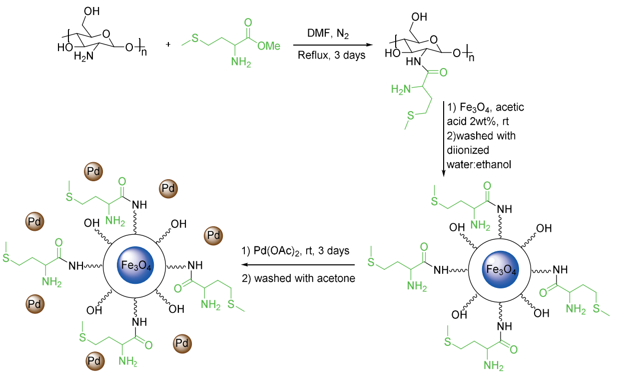
Palladium-catalyzed Heck cross-coupling reactions[29] are some of the most common and practical methods for the construction of new carbon–carbon bonds and are widely used in industrial and academic applications for the synthesis of a large variety of organic substances, bioactive compounds and natural products. Previous studies of Heck arylation were done using harsh conditions such as organic solvents,[30] high temperature,[1] organic bases[31] and long reaction time (or less efficiency for bromobenzene derivatives).[32] Furthermore, reports of Heck arylation at room temperature are rare,[33] so it is highly desirable to design an active and stable catalyst for the reaction in water at room temperature.

Accordingly, in the work reported in this article, we introduced palladium nanoparticles immobilized on magnetic methionine-functionalized chitosan in order to develop a new and highly efficient heterogeneous catalyst for used under green reaction conditions and we evaluated its application in Heck reactions of aryl iodides and aryl bromides in water at room temperature.

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of palladium nanoparticles immobilized on Fe_3O_4–Chitosan (CS)–methionine (ImmPd(0)-MNPs)

As shown in Scheme 1, the route to prepare the catalyst contains three steps. First, CS–methionine was prepared by the reaction between methyl methioninate and chitosan in dimethylformamide (DMF). In the second step, CS–methionine was treated with Fe_3O_4 nanoparticles prepared by mixing of $FeCl_3·6H_2O$ and $FeSO_4$ according to a reported procedure,[34] to obtain Fe_3O_4–CS–methionine as a magnetic substrate. Finally, palladium acetate was grafted into this magnetic support in ethanol to afford ImmPd(0)-MNPs as the final catalyst.



SCHEME 1 Synthetic paths for the preparation of ImmPd-MNPs catalyst

The following methods were used to characterize the catalyst: transmission electron microscopy (TEM); field-emission scanning electron microscopy (FE-SEM); powder X-ray diffraction (XRD); and energy-dispersive X-ray spectroscopy (EDX). Fourier transform infrared (FT-IR) spectroscopy was used for characterizing CS–methionine and Fe_3O_4–CS–methionine. Thermal behavior of the catalyst was also studied using thermogravimetric analysis. The magnetization curve of ImmPd(0)-MNPs indicates the magnetic behavior of the catalyst.

The TEM image of the ImmPd(0)-MNPs catalyst (Figure 1) shows that the Pd nanoparticles with near spherical morphology are accumulated onto the magnetic functionalized chitosan with relatively good monodispersity. The histogram indicating the size distribution of Pd nanoparticles is also shown in Figure 1, constructed according to the data acquired from the TEM image, showing an average size of 6–7 nm. The FE-SEM images in Figure 2 show spherical external morphologies of the catalyst. Also, to determine the Pd content on the catalyst, the catalyst was reacted with concentrated HCl to digest the Pd particles and then analyzed

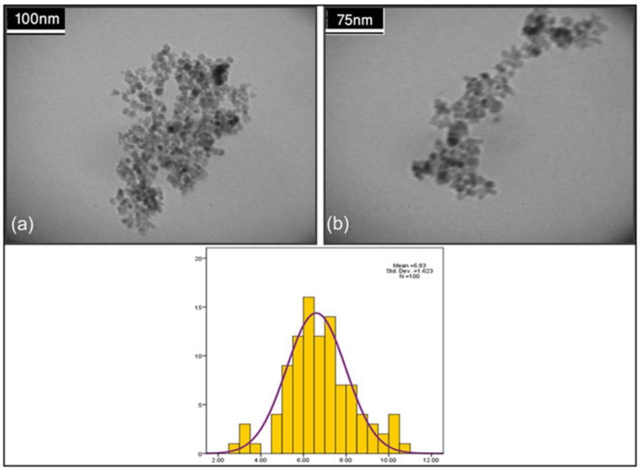


FIGURE 1 (a) TEM image of ImmPd(0)-MNPs catalyst showing the morphology of Pd nanoparticles on the magnetic chitosan support. Beneath is the histogram of the particle size distribution. (b) TEM image of ImmPd (0)-MNPs catalyst after eight recycles

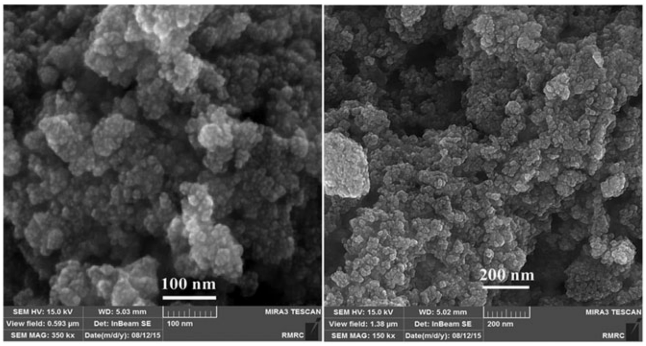


FIGURE 2 FE-SEM images of ImmPd(0)-MNPs catalyst complex

using the inductively coupled plasma (ICP) technique. The amount of palladium is found to be 7.1 ppm (7.1 mg l^{-1}).

The XRD study of ImmPd(0)-MNPs confirms the presence of highly dispersed palladium complexes in the structure of the modified chitosan support. According to Figure 3, a sharp peak at $2\theta = 40°$, which is related to palladium, indicates the crystalline nature of the palladium species. The peaks which are indexed as (111), (200), (220), (311) and (222) indicate the cubic phase of palladium nanoparticles (JCPDS 01–087-0638). As presented in Figure 3, 11 characteristic diffraction peaks ($2\theta = 30.1°$ (220), 35.5° (311), 43.1° (400), 47.2° (331), 53.5° (422), 57.0° (511), 62.6° (440), 75.1° (622), 82.0° (551), 86.8° (642) and 89.8° (731)) can be clearly observed for Fe_3O_4 particles, which are associated with the cubic phase of Fe_3O_4 (JCPDS 01–075-0033).

As clearly observed, according to the EDX spectrum (Figure 4), the presence of palladium is demonstrated on the magnetic chitosan in the ImmPd(0)-MNPs catalyst. The EDX spectrum also indicates other elements, including S, O and Fe, which are present in the Fe_3O_4–CS–methionine substrate.

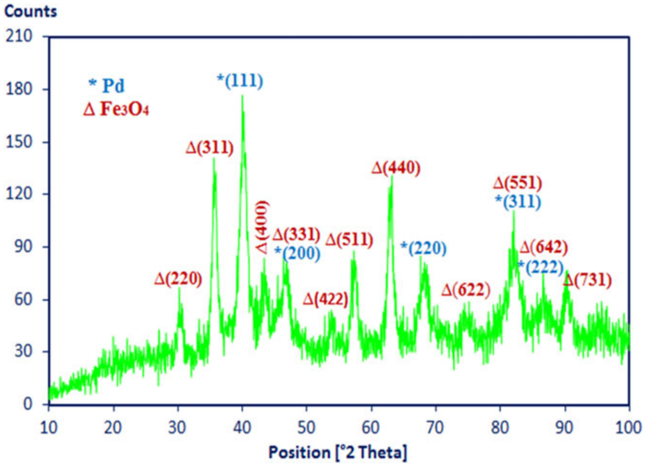


FIGURE 3 XRD pattern of ImmPd(0)-MNPs catalyst

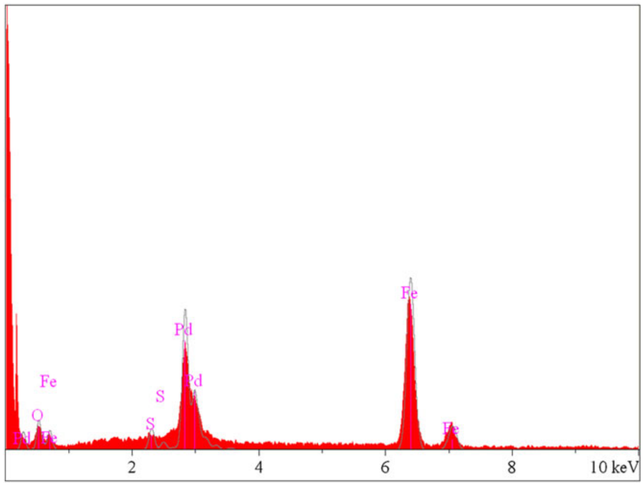


FIGURE 4 EDX spectrum of ImmPd(0)-MNPs catalyst

Comparison among the FT-IR spectra (Figure 5) of pure chitosan, CS–methionine, Fe_3O_4 and the Fe_3O_4–CS–methionine substrate indicates that some absorption bands in the spectrum of Fe_3O_4–CS–methionine are present in those of both chitosan and Fe_3O_4. The FT-IR spectrum of CS–methionine reveals a carbonyl group absorption band, which confirms that methionine has been attached into the chitosan after the reaction between chitosan and methioninate. A typical strong and broad band appears at around 3419 cm^{-1}, related to the stretching vibration of the —OH group, the extension vibration of the N—H group and inter-hydrogen bonds of polysaccharide in the Fe_3O_4–CS–methionine spectrum.[35,36] In addition, the intensity of the band at 1385 cm^{-1} is increased in the spectrum of the CS–methionine material; this is associated with the introduction of additional amine groups.[35] Bands at 3419, 2925, 2354, 1632, 1394, 1064 and 566 cm^{-1} correspond to the bonds in Fe_3O_4–CS–methionine. The band at 566 cm^{-1} is assigned to the Fe—O stretching vibration of Fe_3O_4.[37] In the FT-IR spectrum of CS–methionine, an additional band appears at 1655 cm^{-1}; this band is representative of the (—CON—) carboxyl amide group vibration of the methionine moiety.

TGA was used to investigate the thermal stability of the catalyst (Figure 6). The weight loss for all samples occurring up to 200°C is ascribed to the loss of physically adsorbed solvent molecules and moisture.[30] The mass loss above 200°C in the TGA curve of the magnetic catalyst is related to the decomposition of polysaccharide chain. So, the elevated temperature for chitosan decomposition indicates the high thermal stability of the catalyst.

The magnetization curves of ImmPd(0)-MNPs and Fe_3O_4 indicate the magnetic behavior of ImmPd(0)-MNPs (Figure 7). The two samples demonstrate zero coercivity and remanence on the magnetization curve. The lack of a hysteresis loop denotes the magnetic property and the tendency of the catalyst to be able to be separated efficiently from the

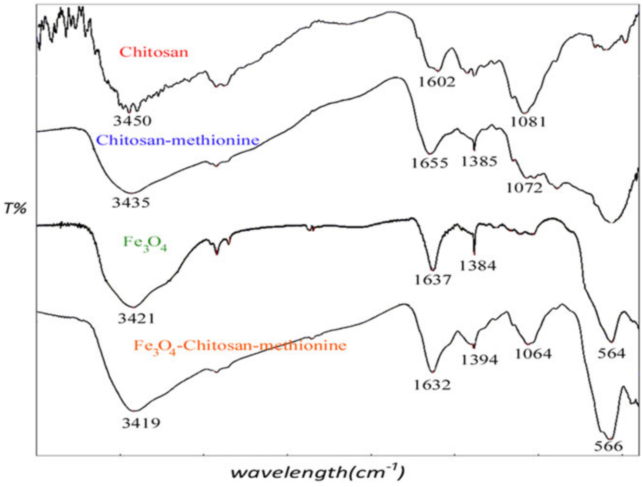


FIGURE 5 FT-IR spectra of pure chitosan, CS–methionine, Fe3O4 and Fe3O4–CS–methionine substrate

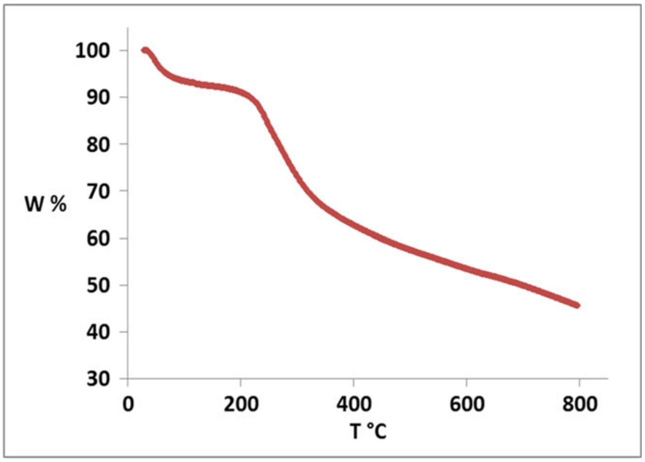


FIGURE 6 Typical TGA curve of ImmPd(0)-MNPs catalyst

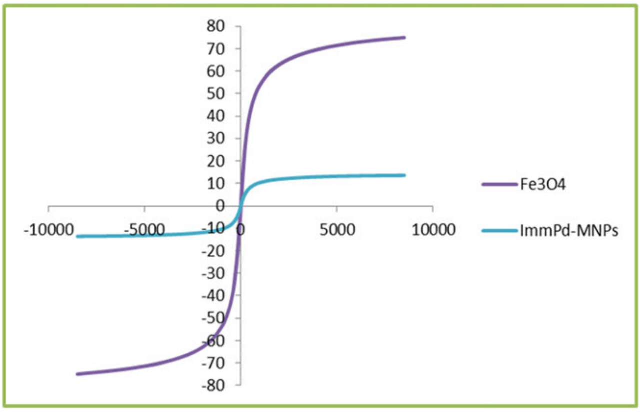


FIGURE 7 Magnetization curves of ImmPd(0)-MNPs catalyst and Fe_3O_4

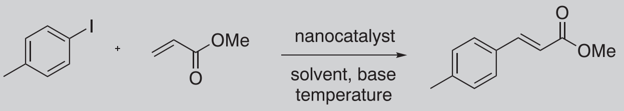
reaction mixture using an external magnetic field. Further, the reduction in the magnetization value of the catalyst in comparison with Fe_3O_4 indicates that the surface of Fe_3O_4 is covered by the attachment of chitosan molecules through their bond formation via their hydroxyl functional groups. Even with this reduction in the saturation magnetization, the catalyst still can be separated simply from solution using an external magnet.

2.2 | Heck reaction catalyzed by ImmPd(0)-MNPs

After characterizing the prepared catalyst, we explored the catalytic properties of ImmPd(0)-MNPs for C─C bond formation via a Heck coupling reaction. In our initial study, we chose the reaction between 4-iodotoluene and methyl acrylate as a model reaction to compare the effects of various conditions such as solvent, base, temperature and quantity of catalyst. The optimization of conditions is summarized in Table 1.

Initially, we chose water–ethanol (1:1) and K_2CO_3 as the media for the Heck reaction of 4-iodotoluene with methyl acrylate under reflux conditions. The reaction proceeds completely after 50 min with a 94% GC yield (Table 1, entry 1). Since our objective was an exceedingly versatile catalyst for room temperature Heck couplings of aryl halides, we were encouraged to observe the ImmPd(0)-MNPs catalyst as significantly active, which permits the room temperature coupling of 4-iodotoluene with methyl acrylate (Table 1, entry 2). Results obtained for other conditions also reveal that the catalyst is highly efficient for Heck coupling. When water is used as the solvent, the product yield does not reduce (Table 1, entry 3) and because of this, water was chosen for this reaction as a green medium. Heck couplings between lipophilic aryl iodides and acrylates, using K_2CO_3 as base and water as solvent, could more successfully be carried out using a phase transfer agent. As expected, when tetrabutylammonium bromide (TBAB) is added to the reaction mixture as an additive, the reaction time is reduced from 5.5 h to 1:5 h to achieve a high yield (Table 1, entry 4). The influence of base on the reaction was also investigated

TABLE 1 ImmPd(0)-MNPs-catalyzed Heck reaction between 4-iodotoluene and methyl acrylate[a]



Entry	Solvent	Base	Temp.	Time (h)	Yield (%)[b]
1	H_2O–ethanol (1:1)	K_2CO_3	Reflux	0.8	94
2	H_2O–ethanol (1:1)	K_2CO_3	r.t.	2	70
3	H_2O	K_2CO_3	r.t.	5.5	90
4[c]	H_2O	K_2CO_3	r.t.	1.5	96
5[d]	**H_2O**	**K_2CO_3**	**r.t.**	**1.5**	**96**
6[c]	H_2O	K_3PO_4	r.t.	2	90
7[c]	H_2O	KOH	r.t.	1.5	94

[a] Reaction conditions: 4-iodotoluene (0.5 mmol), methyl acrylate (0.6 mmol), base (1 mmol), catalyst (0.025 g, 0.34 mol%) and solvent (2 ml).

[b] GC yield.

[c] TBAB (0.5 equiv.) was added as an additive.

[d] Reaction conditions: 4-iodotoluene (0.5 mmol), methyl acrylate (0.6 mmol), base (1 mmol), catalyst (0.015 g, 0.21 mol%), TBAB (0.5 equiv.) and solvent (2 ml).

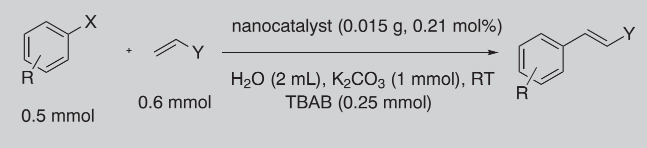
(Table 1, entries 6 and 7). It is evident from Table 1 that different bases show similar effects. Since K_2CO_3 is cheap, acceptable and one of the commonly used bases for the Heck reaction, we decided to use it as the base for the reaction. The model reaction proceeds efficiently when the catalyst loading decreases from 0.025 g (0.34 mol%) to 0.015 g (0.21 mol%) (Table 1, entry 5).

2.3 | Heck reaction of various substrates catalyzed by ImmPd(0)-MNPs

In order to investigate the effect of substituent groups, the Heck arylation of a variety of aryl iodides, aryl bromides and aryl chlorides with various vinylic substrates was examined and different products were obtained in good to excellent yields. Table 2 clearly reveals that the ImmPd(0)-MNPs catalyst is effective for the Heck reaction.

As clearly evident from Table 2, the cross-coupling reaction of iodobenzene derivatives is responsive to both electron-rich and electron-poor substituents and the reaction gives the corresponding products in excellent yields (Table 2, entries 1–6). The Heck reaction of both electron-rich and electron-deficient aryl bromides also proceeds efficiently to provide the desired products with excellent yields (Table 2, entries 7–12). Moderate yields of products are obtained using aryl chlorides in the presence of the ImmPd(0)-MNPs catalyst and also the temperature for the Heck coupling of aryl chlorides is 80°C under reflux conditions (Table 2, entries 13 and 14). It should also be noted that aryl bromides can selectively react with olefin in the presence of aryl chlorides (Table 2, entry 11).

TABLE 2 ImmPd(0)-MNPs-catalyzed Heck reaction between various aryl halides and olefins



Entry	R	X	Y	Time (h)	Yield (%)[a]
1	4-Me	I	CO_2Me	1.5	96
2	4-Me	I	CO_2Bu	2	89
3	4-OMe	I	CO_2Bu	1.5	93
4	4-OMe	I	Ph	2.25	90
5	H	I	CO_2Bu	2	90
6	4-CN	I	CO_2Bu	4.5	86
7	4-OMe	Br	CO_2Bu	6	90
8	4-OMe	Br	Ph	8.75	83
9	4-CH_3CO	Br	CO_2Me	10	61
10	H	Br	CO_2Bu	6.25	85
11	4-Cl	Br	CO_2Me	5	93
12	4-NO_2	Br	Ph	8	80
13[b]	H	Cl	CO_2Bu	5.5	73
14[b]	4-NO_2	Cl	Ph	6	67

[a] Isolated yield.

[b] Reaction conditions: aryl halide (0.5 mmol), olefin (0.6 mmol), K_2CO_3 (1 mmol), TBAB (0.25 mmol), catalyst (0.02 g, 0.28 mol%) and H_2O (2 ml) under reflux.

Compared with previous literature on the Heck coupling reaction, the marked features of our method are:

- the reaction system is simple;
- removal of toxic reagents and homogeneous catalysts;
- the yields of the products are high;
- water is used as a green medium;
- the ImmPd-MNPs catalyst can be easily recovered using an external magnet; and
- the reactions proceed at room temperature for both aryl iodides and aryl bromides.

2.4 | Recycling of ImmPd(0)-MNPs catalyst for heck reaction

The level of reusability is one of the significant factors for heterogeneous catalysts. To examine the reusability of the catalyst, the reaction of 4-iodotoluene with methyl acrylate under optimized reaction conditions was used. When the reaction was completed, the catalyst was separated using an external magnet, washed with water and acetone (3 × 5 ml) and dried at room temperature to be used in the next run. The recycled catalyst could be reused eight times and no significant decrease was observed in its activity (Figure 8). This is also quantitatively supported by ICP analysis. ICP analysis after eight cycles of recycling of the catalyst shows that only a small amount of palladium metal is removed from the Fe_3O_4–CS–methionine support. In order to determine whether the observed catalytic activity is from the supported palladium nanoparticles on the Fe_3O_4–CS–methionine and not from leached palladium in solution, we performed the reaction of 4-iodotoluene with methyl acrylate under the optimized reaction condition. After completion of the reaction, the catalyst was removed using an external magnet and the obtained aqueous solution from the extraction was applied

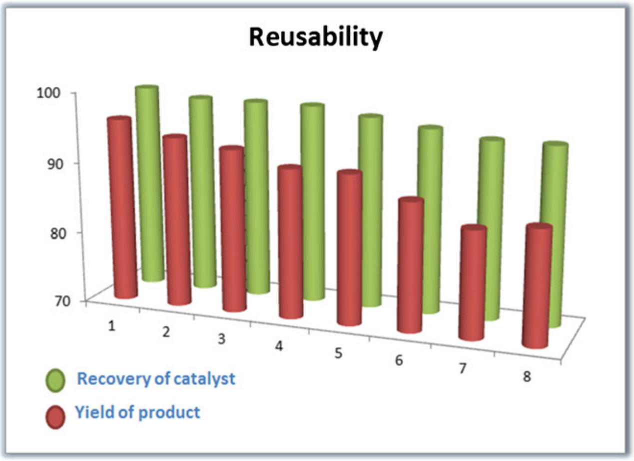


FIGURE 8 Catalyst reusability test of the ImmPd(0)-MNPs catalyst

for the next reaction between 4-iodotoluene with methyl acrylate under optimized conditions. After a similar purification process, the isolated yield of products was less than 8%. ICP analysis of the aqueous solution obtained from extraction shows that only 0.3 ppm of palladium is in this solution. TEM images were obtained and ICP analysis was conducted of the recovered catalyst to study the possible changes in palladium particle morphology/size and palladium content on the catalyst surface in comparison with fresh catalyst. As shown in Figure 1(b), the TEM image of the catalyst indicates that the morphology and size of the catalyst are negligibly changed after eight times of recycling. Furthermore, the ICP analysis data for the reused catalyst after recycling eight times demonstrate that during the reaction process only a small amount of palladium nanoparticles (0.3 ppm) is lost. These results verify that the high catalytic activity is related to the ImmPd(0)-MNPs catalyst and not to leached palladium.

3 | CONCLUSIONS

In summary, we have demonstrated the preparation, characterization and application of a new and high-performance catalyst system for the coupling of aryl iodides and bromides with olefins in a green environment. The yields for the alkene derivatives, with respect to reaction time, show that the catalyst has excellent activity. Moreover, the ImmPd(0)-MNPs catalyst is very stable and can be recovered easily using an external magnet without loss of activity. We believe that this catalyst provides great potential for further convenient applications in other palladium transformations in the future.

4 | EXPERIMENTAL

4.1 | Chemicals, instrumentation and analysis

All chemical reagents were purchased from Merck and Aldrich and were used without further purification. Chitosan was purchased from Acros Organics and its molecular weight was 1×10^5–3×10^5 g mol^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker (250 and 62.9 MHz) Avance DRX in pure $CDCl_3$ solvent with tetramethylsilane as internal standard. FT-IR spectra were obtained as KBr pellets with a JASCO 680 Plus spectrophotometer for characterization of the ImmPd(0)-MNPs catalyst. Magnetic measurement was done with a vibrating sample magnetometer at 0.0001–50 emu. TEM (Zeiss-EM10C, 80 kV) and FE-SEM (MIRA3 TESCAN) were used to characterize the ImmPd-MNPs catalyst. TGA of the catalyst was conducted using a lab-made TGA instrument. XRD (D8, Advance, Bruker) was used for characterization of the ImmPd(0)-MNPs catalyst. Reaction monitoring was accomplished using TLC or GC (BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm). Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

4.2 | Catalyst preparation

4.2.1 | Preparation of CS–methionine

Methyl methioninate (10 mmol, 1.28 g) was added to a flask containing chitosan (1 g) in DMF (40 ml). The resulting mixture was refluxed for three days under nitrogen atmosphere. The product was allowed to cool to room temperature followed by separation to afford the methionine-functionalized chitosan. Then, the product was collected and washed with methanol several times to remove the impurities and dried.

4.2.2 | Preparation of Fe_3O_4–CS–methionine

Fe_3O_4 nanoparticles were prepared without using any plugging agent or surfactant via conventional co-precipitation of iron(II) sulfate and iron(III) chloride according to a reported procedure.[34] After sonication, Fe_3O_4 nanoparticles (2.1 g) were treated with CS–methionine (0.7 g) in 2 wt% acetic acid solution. The resulting mixture was sonicated for 20 min and then stirred for 30 min at room temperature. The product was collected and washed with ethanol and deionized water several times. After drying in a vacuum oven at 70°C overnight, the Fe_3O_4–CS–methionine support was obtained as a dark solid.

4.2.3 | Preparation of ImmPd(0)-MNPs

To a mixture of magnetic Fe_3O_4–CS–methionine (0.5 g) in ethanol (20 ml) was added $Pd(OAc)_2$ (0.05 g) and stirred for three days at room temperature. Then, the powder was filtered and washed with acetone several times. The ImmPd (0)-MNPs catalyst was obtained as a black powder.

4.3 | General procedure for heck reaction in presence of ImmPd(0)-MNPs catalyst

In a typical experiment, to a flask containing a mixture of aryl halide (0.5 mmol), olefin (0.6 mmol), TBAB (0.5 equiv.) and K_2CO_3 (1 mmol) in 2 ml of water, ImmPd(0)-MNPs catalyst (0.015 g, 0.21 mol%) was added and stirred in room temperature for the time specified in Table 2. The reaction was monitored by TLC or GC. After consumption of aryl halide, the mixture was cooled to room temperature and filtered. The remaining solid was washed with water and acetone (3 × 5 ml) in order to separate the catalyst. After the extraction of the reaction mixture with ethyl acetate (3 × 5 ml), the organic extract was dried over $CaCl_2$. The products were purified by column chromatography (*n*-hexane–ethyl acetate) to achieve the desired purity.

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